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Synthesis and Characterization of Diorganotin(IV) Derivatives of 2-Mercaptopyridine and Crystal Structure of Diphenyl Pyridine-2-thiolatochlorotin(IV)

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Diorganotin(IV) derivatives of 2-mercaptopyridine (HSPy), $R_2Sn(SPy)_2$, $R_2SnCl(SPy)$ ($R=Me$, iPr, nBu, tBu, Cy, Ph) and $Cy_2SnBr(SPy)$, were obtained from R_2SnX_2 ($X=Cl$, Br) and NaSPy.

$Ph_2SnCl(SPy)$ crystals, as determined by single-crystal X-ray diffraction, are monoclinic in the space group *P*2_1/n. Tin forms with the bidentate SPy ligand a four-membered chelate ring with a short NSnS bite angle of 64.8(1)° leading to a heavily distorted trigonal-bipyramidal environment about tin. Apical Cl–Sn–N angle = 156.1(1)°; equatorial C–Sn–C angle = 121.9(2)°. From ^{119}Sn Mössbauer and IR data, analogous structures are inferred for the other solid compounds $R_2SnX(SPy)$, and distorted octahedral molecular structures for the solid compounds $R_2Sn(SPy)_2$ with R in the *trans* position, and sulfur atoms and nitrogen-donor atoms each in *cis* positions. According to IR and ^1H, ^{13}C and ^{119}Sn NMR data, the solid-state molecular structures are retained in chloroform solution.

Keywords: Organotin, 2-mercaptopyridine, pyridine-2-thiolato complexes, Mössbauer, IR, NMR, crystal structure

INTRODUCTION

Diorganotin sulfur compounds such as diorganotin dithiolates $R_2Sn(SR')_2$ have been found to be able to act as stabilizers for polymers such as poly(vinyl chloride), and consequently a huge number of diorganotin dithiolates have been prepared and tested for possible applications.[1] In contrast, the structure of these compounds has not found broad interest and only a few X-ray structure determinations of such compounds are known. In continuation of former work on organotin derivatives of mercaptocarboxylic acids,[2–4] in which the mercapto group successfully competes with the functional oxygen group, we started to study organotin derivatives of ligands containing nitrogen donors in addition to a mercapto group. The behavior of such compounds is also interesting, considering the possible support of functional mercapto groups in biological systems by neighboring nitrogen functions, and remembering that the high affinity of mercapto groups for tin was inferred to be a possible cause of the toxicity of organotin compounds bonding to mercapto groups in enzymes and blocking their active centres; moreover, thiol sulfur and heterocyclic nitrogen are thought to coordinate tin centers in rat and cat hemoglobins.[5,6]

In this paper we report on a study of the title compounds, of which only a few have been described in the literature.

EXPERIMENTAL

Synthesis of diorganotin(IV) derivatives of 2-mercaptopyridine

The diorganotin dihalides were prepared according to procedures given in Refs 7–10. HSPy was a product of Fluka Chemie AG; other reactants and solvents were commercial products and were purified and dried as usual.[11] All reactions were carried out under stirring in a dry nitrogen atmosphere.

The new compounds **1–15**, listed in Table 1, were prepared according to one of the following methods.

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Table 1 Analytical data for diorganotin(IV) derivatives of 2-mercaptopyridine (HSPy)

Compound		Method	Yield (%)	M.p. [dec] (°C)	Mol. wt in $CHCl_3$: Found (Calcd)	Analysis (%): Found (Calcd.) C	H	N	Hal
$Me_2Sn(SPy)_2$	**1**	A	79	140[a]	342	38.5	3.9	7.8	—
				[203]	(369)	(39.0)	(3.8)	(7.6)	
$iPr_2(SPy)_2$	**2**	B	65	154	441	45.5	5.4	6.6	—
				[240]	(425)	(45.2)	(5.2)	(6.6)	
$nBu_2Sn(SPy)_2$	**3**	A	82	40[b]	436	46.3	5.9	6.1	—
				[240]	(453)	(47.7)	(5.8)	(6.2)	
$iBu_2Sn(SPy)_2$	**4**	A	56	107	460	47.6	5.9	6.2	—
				[225]	(453)	(47.7)	(5.8)	(6.2)	
$tBu_2Sn(SPy)_2$	**5**	A	88	175	448	47.5	5.6	5.9	—
				[210]	(453)	(47.7)	(5.8)	(6.2)	
$Cy_2Sn(SPy)_2$	**6**	A	88	155[c]	469	52.5	6.2	5.5	—
				[238]	(505)	(52.3)	(6.0)	(5.5)	
$Ph_2Sn(SPy)_2$	**7**	A	81	180[d]	472	53.6	3.8	5.6	—
				[325]	(493)	(53.6)	(3.7)	(5.7)	
$Me_2SnCl(SPy)$	**8**	C	61	49	317/261[e]	28.5	3.4	4.8	11.9
					(294)	(28.6)	(3.4)	(4.8)	(12.0)
$iPr_2SnCl(SPy)$	**9**	D	80	66	369	37.4	5.2	3.9	10.2
				[174]	(350)	(37.7)	(5.2)	(4.0)	(10.1)
$nBu_2SnCl(SPy)$	**10**	E	88	Oil	362	41.2	5.8	3.9	9.2
					(379)	(41.3)	(5.9)	(3.7)	(9.4)
$iBu_2SnCl(SPy)$	**11**	E	92	26	372	41.0	5.9	4.1	9.6
					(379)	(41.3)	(5.9)	(3.7)	(9.4)
$tBu_2SnCl(SPy)$	**12**	A	63	[127–130]	372	40.5	6.2	3.6	9.3
					(379)	(41.3)	(5.9)	(3.7)	(9.4)
$Cy_2SnBr(SPy)$	**13**	A	87	[139–142]	477	42.7	5.5	3.0	16.8
					(475)	(43.0)	(5.5)	(3.0)	(15.9)
$Cy_2SnCl(SPy)$	**14**	A	66	133	430	47.6	6.4	3.2	8.1
				[207]	(431)	(47.4)	(6.1)	(3.3)	(8.2)
$Ph_2SnCl(SPy)$	**15**	A	90	110	388/419[e]	48.7	3.4	3.3	8.8
				[225]	(419)	(48.8)	(3.4)	(3.4)	(8.5)

Abbreviation: SPy, pyridine-2-thiolate. [a] M.p. (°C) 137–138,[22] 139.[21] [b] M.p. (°C) 37–39,[22] 37–38.[23] [c] M.p. (°C) 156–157.[23] [d] M.p. (°C) 170 [dec],[22] 171–172.[23] [e] Solvent: DMSO.

Method A

NaOMe (4 mmol) in MeOH (0.5 M solution, 8 ml) was added to 4 mmol HSPy (0.44 g). After dissolution, 50 ml of chloroform ($CHCl_3$) was added; then, over a period of 10 min, either 0.2 mmol R_2SnCl_2 in 20 ml $CHCl_3$ [for preparation of $R_2Sn(SPy)_2$] or 0.4 mmol R_2SnCl_2 in 40 ml $CHCl_3$ [for preparation of $R_2SnCl(SPy)$] was added. After the mixture had been stirred for 24 h at room temperature, the solvent was removed at 20 °C, and the residue was extracted twice, first with 40 ml then with 20 ml $CHCl_3$. The volume of the extract was reduced to 5–10 ml. Petroleum ether was added until the solution became turbid, and then the mixture was kept for crystallization for 12 h at −30 °C. The product was filtered and dried in vacuum.

Method B

The procedure was analogous to that of method A, but the extract was brought to dryness. The residue was treated with 10 ml n-pentane to leave compound **2**, which after filtration was dried in vacuum.

Method C

A solution of 10 mmol NaSPy in 20 ml methanol was prepared according to method A. Methanol (10 ml) was added instead of $CHCl_3$ and the solution was reacted with 10 mmol Me_2SnCl_2 in 50 ml $CHCl_3$ under stirring for 24 h at room temperature. The solvent was removed in vacuum, the residue was extracted with 50 ml $CHCl_3$ and the extract was brought to dryness. n-Pentane (20 ml) was added to the remaining oil followed at

Table 2 Atomic coordinates and equivalent isotropic displacement parameters ($Å^2 \times 10^4$)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_ia_j$

Atom	x	y	z	U_{eq}
Sn(1)	0.18092(3)	0.05194(2)	0.23846(2)	358
Cl(1)	−0.0077(2)	0.16358(7)	0.2549(1)	556
C(11)	0.3788(5)	0.1008(3)	0.3560(3)	404
C(12)	0.5305(7)	0.0679(3)	0.3679(5)	652
C(13)	0.6514(7)	0.0998(4)	0.4480(5)	823
C(14)	0.6304(7)	0.1663(4)	0.5147(4)	688
C(15)	0.4838(7)	0.1993(4)	0.5021(4)	630
C(16)	0.3590(6)	0.1681(3)	0.4227(4)	481
C(21)	0.0445(5)	−0.0510(2)	0.2758(3)	373
C(22)	−0.0477(6)	−0.0358(3)	0.3512(5)	561
C(23)	−0.1447(6)	−0.0978(3)	0.3757(5)	625
C(24)	−0.1504(6)	−0.1768(3)	0.3255(5)	597
C(25)	−0.0603(6)	−0.1930(3)	0.2519(4)	592
C(26)	0.0379(6)	−0.1308(3)	0.2277(4)	463
S(1)	0.1597(2)	0.08630(8)	0.0462(1)	495
N(1)	0.3267(5)	−0.0401(2)	0.1442(3)	437
C(31)	0.2733(5)	−0.0043(3)	0.0438(4)	407
C(32)	0.3072(6)	−0.0384(3)	−0.0498(4)	519
C(33)	0.3991(7)	−0.1096(3)	−0.0391(5)	631
C(34)	0.4568(7)	−0.1463(3)	0.0628(5)	640
C(35)	0.4168(6)	−0.1106(3)	0.1531(4)	536

−30 °C by a minimum amount of diethyl ether to avoid formation of two phases. Compound **8** crystallized after several months of standing at −30 °C. On addition of seed crystals, compound **8** crystallized in a few hours. However, it then contained inclusions of solvents which could be removed by careful melting.

Method D

$(iPr)_2SnCl_2$ (1 mmol) and compound **2** (1 mmol) were heated in 50 ml $CHCl_3$ under reflux for 24 h. The solvent was removed and the residue was dissolved in 10 ml n-pentane. Crystallization of compound **9** started on scratching with a glass rod.

Method E

The procedure was analogous to that of method B, but an oil remained which was treated in high vacuum to remove residual solvent. Compound **11** crystallized only after several months of standing at −10 °C.

Characterization of compounds 1–15

Infrared (IR) spectra of solids (KBr pellets) were recorded on a Bruker FTIR spectrometer IFS 113 V, and IR spectra of solutions (cell with KBr plates, 25 µm) were obtained on a Perkin-Elmer PE 580 B grating spectrometer. Raman spectra were obtained with a Coderg PHO laser-spectrometer (glass capillaries, 514.5–647.1 nm, according to the sensitivity of the sample). NMR spectra were recorded on a Bruker AM 300 or Bruker AC 200 spectrometer at 37 °C. Tetramethylsilane and tetramethylstannane were used as internal standards. The Mössbauer spectra were measured with the apparatus and techniques described in previous papers.[12, 13] Molecular weights were determined osmometrically. Melting points were determined with a Büchi SMp 20 apparatus, and decomposition temperatures (both uncorrected) by DTA/TG measurements with a Mettler Vacuum-Thermoanalyzer T1 (reference: Al_2O_3, 25 °C; N_2, 6 °C min^{-1}; Pt/PtRh thermoelement).

Single crystals of $Ph_2SnCl(SPy)$ (**15**) were obtained by crystallization from $CHCl_3$; petroleum ether was added at −30 °C until the solution started to become turbid. A crystal of dimensions 0.24 mm × 0.28 mm × 0.32 mm sealed in a glass capillary under argon was used to obtain cell data, and subsequently for intensity measurements. Crystal data were as follows: $M_r = 418.51$, $a = 8.735(3)$ Å, $b = 15.746(5)$ Å, $c = 12.519(4)$ Å, $\beta = 103.72(3)°$, $V = 1673(1)$ $Å^3$, $Z = 4$, $D_x = 1.662$ mg m^{-3}, monoclinic, space group $P2_1/n$.

The intensities of 3404 ($1.5° \leq \theta \leq 25.0°$; $-11 \leq h \leq 0$; $0 \leq k \leq 19$; $-15 \leq l \leq 15$) reflections were measured on a Nicolet R3m/V diffractometer, graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 1.81$ mm^{-1}, $T = 291(1)$ K; $F(000) = 824$, $\omega/2\theta$ scans, scan speed 1.5–14.6° min^{-1}. Lattice parameters are taken from least-squares fit with 30 reflections up to $2\theta = 30.5°$. The data were corrected for Lorentz polarization but not for absorption effects. After averaging equivalent reflections, 2850 unique reflections ($R_{int} = 0.139$) remained from which 2613 reflections with $F \geq 3.0\,\sigma(F)$ were used for the structure determination via the Patterson function, $\Delta\rho$ maps and full-matrix least-squares refinements with anisotropic temperature factors for all non-H atoms and a common isotropic temperature factor for H atoms, which were placed in geometrically calculated positions (C–H, 0.96 Å). Complex neutral-atom scattering factors and real and imaginary dispersion terms were taken from Ref. 14. Refinement on F with 2613 reflections and 191 refined parameters converged to $S = 1.053$, $R = 0.0375$, $wR = 0.0504$, $(\Delta/\sigma)_{max} = 0.032$ (no extinction correction). The largest peak in the final ΔF map was ± 0.5 e Å^{-3}. The following programs were used: PARST,[15] SHELX76,[16] SHELXTL PLUS,[17] PLATON,[18] MISSYM[19] and SCHAKAL.[20]

Final fractional atomic coordinates are listed in Table 2, selected bond distances and angles in Table 3. Full listings of atomic coordinates and thermal parameters are available upon request from the authors.

RESULTS AND DISCUSSION

The title compounds listed in Table 1 were prepared by the reaction of the appropriate diorganotin dichloride with the sodium salt of 2-mercaptopyridine, HSPy, in $CHCl_3$ with yields up to about 90%, according to Eqn [1]:

$$R_2SnCl_2 + n\,NaSPy \rightarrow R_2SnCl_{2-n}(SPy)_n + n\,NaCl \qquad (n = 1, 2) \qquad [1]$$

Compounds **1**,[21,22] **3** and **7**[22] had been prepared earlier in a similar way in ethanol (EtOH) as solvent. Also, reaction of R_2SnO and HSPy in a 1:2 mole ratio in toluene/EtOH was used for synthesis of $R_2Sn(SPy)_2$, and compounds **3**, **6** and **7** were obtained with yields of 70–77%.[23] We also tried to employ this procedure to prepare compounds **1** and **7** by neutralization of equimolar amounts of R_2SnO (R = Me, Ph) and HSPy in MeOH under reflux in the presence of 2,2-dimethoxypropane, but yields were low (**1**, 30%; **7**, 45%) even after 30 h reaction time. We had already obtained compounds **1** and **7** in an earlier study[24] by reaction of R_2SnCl_2 (R = Me, Ph) and HSPy in a $CHCl_3$/water emulsion to which ammonia was added in order to favor the thiolate concentration (SPy^-) and to neutralize HCl. However, the isolation of the products was less straightforward and yields (**1**, 82%,[24] 41%; **7**: 79%,[24] 45%) were not generally reproducible. Neither the latter reaction nor the neutralization reaction could be employed successfully for preparing $R_2SnX(SPy)$ compounds. In any case it is advantageous first to shift the thion/thiol (SPyH/HSPy) equilibrium[25-28] existing in solutions of mercaptopyridine and to increase the thiolate concentration.

Table 3 Bond distances and bond angles

Atoms	Distance (Å)	Atoms	Distance (Å)
Sn(1)–Cl(1)	2.451(2)	N(1)–C(31)	1.355(6)
Sn(1)–C(11)	2.131(4)	N(1)–C(35)	1.352(6)
Sn(1)–C(21)	2.127(4)	C(31)–C(32)	1.384(7)
Sn(1)–S(1)	2.431(2)	C(32)–C(33)	1.367(8)
Sn(1)–N(1)	2.413(4)	C(33)–C(34)	1.386(8)
S(1)–C(31)	1.741(5)	C(34)–C(35)	1.377(9)

Atoms	Angle (°)	Atoms	Angle (°)
S(1)–Sn(1)–N(1)	64.8(1)	Sn(1)–C(21)–C(22)	117.5(3)
C(21)–Sn(1)–N(1)	92.2(2)	Sn(1)–S(1)–C(31)	85.6(2)
C(21)–Sn(1)–S(1)	118.1(1)	Sn(1)–N(1)–C(35)	145.0(3)
C(11)–Sn(1)–N(1)	96.8(2)	Sn(1)–N(1)–C(31)	95.6(3)
C(11)–Sn(1)–S(1)	117.6(1)	C(31)–N(1)–C(35)	118.8(4)
C(11)–Sn(1)–C(21)	121.9(2)	S(1)–C(31)–N(1)	113.4(3)
Cl(1)–Sn(1)–N(1)	156.1(1)	N(1)–C(31)–C(32)	121.9(4)
Cl(1)–Sn(1)–S(1)	91.63(6)	S(1)–C(31)–C(32)	124.6(4)
Cl(1)–Sn(1)–C(21)	96.0(1)	C(31)–C(32)–C(33)	118.4(5)
Cl(1)–Sn(1)–C(11)	97.8(1)	C(32)–C(33)–C(34)	120.6(5)
Sn(1)–C(11)–C(16)	119.7(3)	C(33)–C(34)–C(35)	118.4(5)
Sn(1)–C(11)–C(12)	122.3(3)	N(1)–C(35)–C(34)	121.8(5)
Sn(1)–C(21)–C(26)	124.2(3)		

C–C distances and C–C–C angles in the phenyl rings are in the usual range.

Table 4 ^{119}Sn Mössbauer parameters, at 77 K, of diorganotin(IV) derivatives of 2-mercaptopyridine

Compound^a	δ^b (mm s^{-1})	ΔE^c (mm s^{-1})	Γ_1^d (mm s^{-1})	Γ_2^d (mm s^{-1})
1	1.34	2.55	0.83	0.91
3	1.51	2.87	0.82	0.77
5	1.71	2.65	0.84	0.87
6	1.57	2.82	0.83	0.85
7	1.32	2.31	0.93	0.84
8	1.31	2.78	0.94	0.90
12	1.66	2.98	0.84	0.85
14	1.54	2.94	0.82	0.95
15	1.22	2.58	0.84	0.94

[a] Sample thickness was about 0.50 mg ^{119}Sn cm^{-2}. [b] Isomer shift relative to Ca^{119}SnO$_3$ at room temperature. [c] Nuclear quadrupole splitting. [d] Full width at half-height of the resonant peaks, at greater (Γ_1) and lesser (Γ_2) velocity than the spectrum centroid.

The colorless or slightly yellow products are insensitive to water, light and air. They decompose slowly on prolonged storage at room temperature. Both types of compounds are insoluble in water. With dilute NaOH solution they react to give R_2SnO. The $R_2Sn(SPy)_2$ compounds **1**–**7** are soluble in $CHCl_3$, moderately soluble in CCl_4 and polar solvents such as MeOH or EtOH, and only slightly soluble in $(C_2H_5)_2O$ and in nonpolar solvents such as n-pentane. The $R_2SnCl(SPy)$ compounds **8**–**15** show similar solubilities, but they are somewhat more soluble in polar organic solvents and show high solubility in coordinating solvents such as DMSO. In contrast, the dithiolates $R_2Sn(SPy)_2$ are only slightly soluble in DMSO. Thus, compound **5** precipitated from $CHCl_3$ solution on addition of DMSO, and it may be inferred that appreciable Sn←DMSO coordination does not occur. Molecular weight measurements (Table 1) showed all the compounds to be monomeric in $CHCl_3$ solution.

Structure in the solid state

Mössbauer spectra were measured for some representative compounds of the series $R_2Sn(SPy)_2$

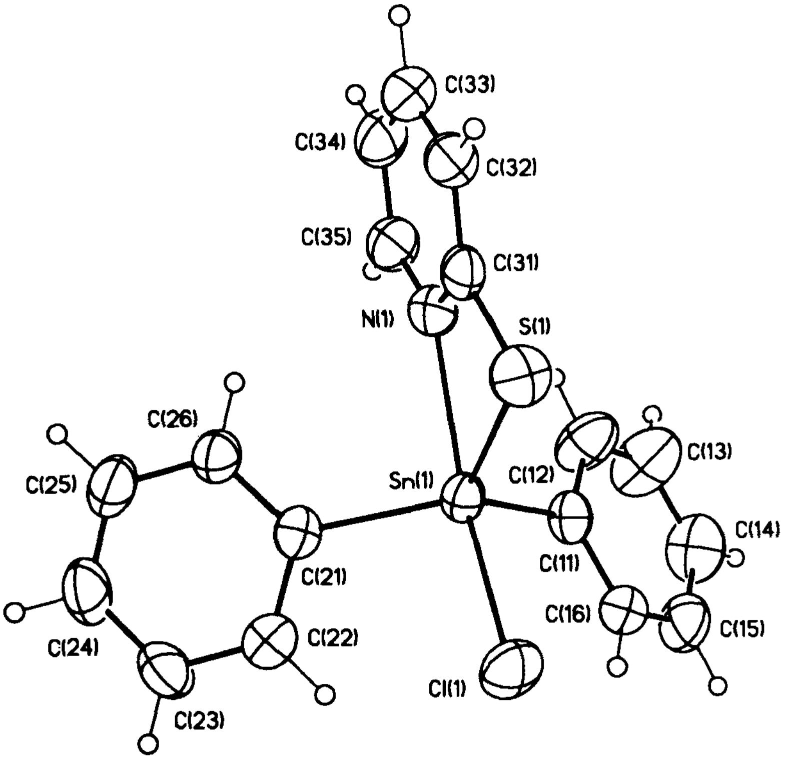


Figure 1 Structure of diphenyl pyridine-2-thiolatochlorotin(IV) (**15**): view (SHELXTL Plus graphic) of the molecule showing atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries. Hydrogen atoms are represented as spheres of arbitrary radii.

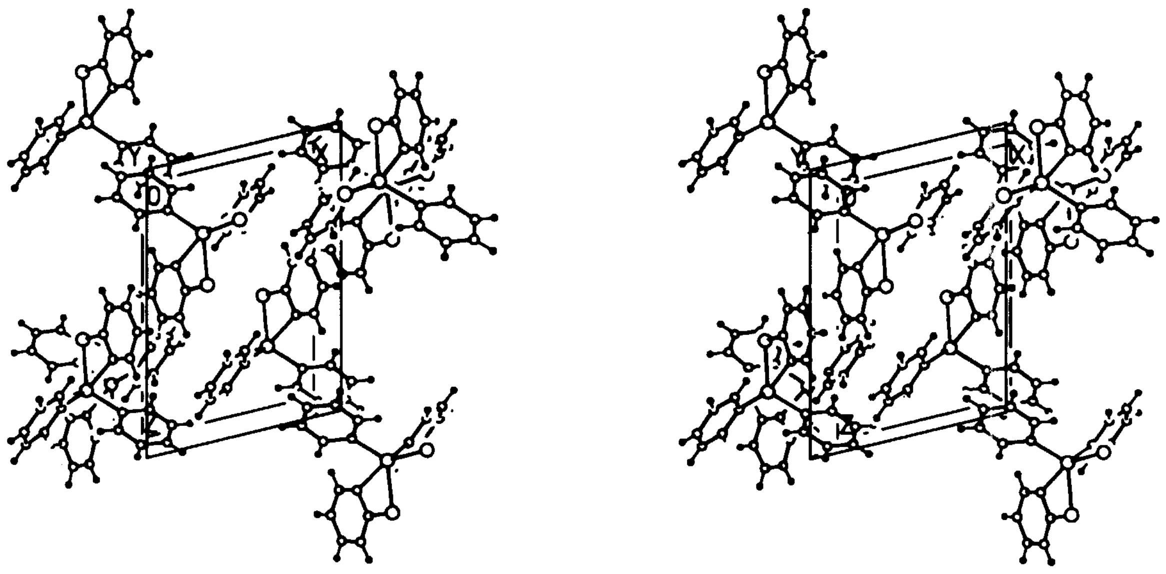
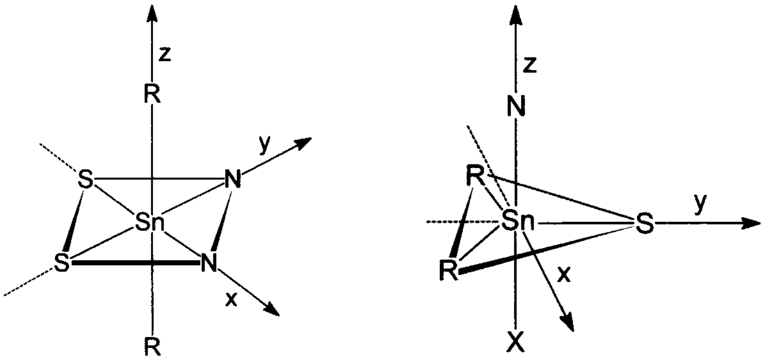


Figure 2 Structure of diphenyl pyridine-2-thiolatochlorotin(IV) (**15**): stereoscopic view (SHELXTL Plus graphic) of the unit cell.

and $R_2SnX(SPy)$; the parameters are reported in Table 4. Symmetrical spectra were obtained, considering the line widths as well as the area of the percentage resonance effect of the peaks. Compared with the natural line width, 0.65 mm s^{-1}, the spectra are characterized by narrow lines, indicative of single tin sites. The isomer shifts, δ, are in the range expected for diorganotin(IV) derivatives,[29] while the quadrupole splitting values, ΔE, define the geometry of the tin environment. Structural data are available for one $R_2SnX(SPy)$ compound (**15**, this work), and for three $R_2Sn(SPy)_2$ type compounds (**1**,[30] **6**[23] and **7**[31]). The latter contain six-coordinated tin and have a skew-trapezoidal bipyramidal structure, common also to di-n-butyl bis(2-thiolato-5-nitropyridine)tin(IV).[32] The sulfur atoms as well as the nitrogen-donor atoms are each in the *cis* position and lie with tin approximately in a plane. The N–Sn–N and S–Sn–S angles measure about 150° and 90°, respectively, and the C–Sn–C angles range from 125° to 129°. The molecules of the $R_2Sn(SPy)_2$ compounds **1**, **6** and **7** deviate very strongly from ideal octahedral geometry around tin, and compound **6** has also been considered to have a strongly distorted



R = Alk, QS_{calc} = 2.80, η = 0
R = Ph, QS_{calc} = 2.48, η = 0

R = Alk, QS_{calc} = - 2.94, η = 0.57
R = Ph, QS_{calc} = - 2.57, η = 0.46

Figure 3 Regular octahedral and trigonal-bipyramidal structures of $R_2Sn(SPy)_2$ and $R_2SnX(SPy)$, respectively, assumed in the point-charge model estimate of the nuclear quadrupole splitting, ΔE. The directions of the principal components of the diagonalized electric field tensor (x, y, z) are shown.

Table 5 Infrared spectral data for diorganotin(IV) derivatives of 2-mercaptopyridine (HSPy), HSPy, and PySSPy (**16**)

	ν(C—C/C—N) (cm^{-1})				δ(C—H)[b] (cm^{-1})			ring[c] (cm^{-1})
Compound[a]	A	B	C	D	E	F	G	H
SPyH[d]	1613 vs	1574 vs[e]	1495 s	1439 vs	903 s	742 vs	729 vs	617 s
16[f]	1569 vs	1556 vs	1443 vs	1417 vs	766 sh	754 vs	715 vs	616 s
1[g]	1579 vs	1553 vs	1450 s	1415 vs	767 s	748 vs	725 s	627 m
2[g]	1573 s	1549 s	1444 s	1413 vs	756 s		724 s	629 m
3	1578 vs	1550 vs	1444 s	1416 vs	755 vs		726 vs	628 m
4	1576 vs	1551 vs	1452 s	1414 vs	762 s	750 vs	725 vs	628 m
5	1577 vs	1550 vs	1449 vs	1416 vs	754 vs		726 vs	628 s
6	1577 vs	1550 s	1446 s	1415 vs	753 s		725 s	627 m
7[g]	1578 vs	1555 w	1449 m	1418 s	758 sh	751 s	728 s	629 vw
8	1584 vs	1555 vs	1448 vs	1425 vs	776 vs	759 vs	726 vs	640 s
9[h]	1583 vs	1554 vs	1448 vs	1422 vs	759 vs, b		727 vs	638 s
10	1583 vs	1555 s	1453 s 1447 s	1421 vs	785 s	760 vs	728 vs	638 s
11	1585 vs	1556 vs	1450 vs	1423 vs	759 vs		726 s	635 m
12	1584 vs	1554 vs	1451 vs	1422 vs	767 vs		729 vs	635 s
13	1584 vs	1555 vs	1449 vs	1425 vs	766 vs		727 s	637 s
14	1583 vs	1555 vs	1449 vs	1425 vs	767 s		727 m	637 m
15	1584 vs	1551 s	1447 vs	1422 vs	761 vs		734 vs	637 s

[a] A reference in this column describes earlier measurements. [b] 'Out-of-plane' deformation. [c] Ring deformation. [d] Ref. 28. [e] δ(N—H). [f] Ref. 21. [g] Ref. 22. [h] Measured as neat oil between KBr plates.

tetrahedral geometry with two weak additional N→Sn coordination bonds.[23] The X-ray structure determination of compound **15** (see below) also reveals a considerable deviation from the ideal geometry around tin (Figs 1 and 2). The distortion of the trigonal bipyramid is clearly an effect of the presence of only one ligand with a rigid chelating geometry causing a short N–Sn–S 'bite' [bond angle 64.8(1)°].

On a fingerprint basis, the similarity of the Mössbauer ΔE values indicate that the complexes in each series of compounds $R_2Sn(SPy)_2$ and $R_2SnX(SPy)$ have the same hexacoordinated and pentacoordinated structure, respectively. To rationalize experimental values, we carried out point-charge model calculations.[29] We assumed a regular *trans*-octrahedral structure for the complexes $R_2Sn(SPy)_2$ and a regular trigonal bipipyramidal one for the complexes $R_2SnX(SPy)$, as shown in Fig. 3. The partial quadrupole splitting (pqs) values used, in mm s^{-1}, are: $([\mathrm{Alk}]\text{-}[\mathrm{C}])_{\mathrm{oct}} = -1.03$, $([\mathrm{Ph}]\text{-}[\mathrm{Cl}])^{\mathrm{oct}} = -0.95$, $([\mathrm{S}]\text{-}[\mathrm{Cl}])^{\mathrm{oct}} = -0.56$, $([\mathrm{N}]\text{-}[\mathrm{Cl}])^{\mathrm{oct}} = -0.10$, $[\mathrm{Alk}]^{\mathrm{tbe}} = -1.13$, $[\mathrm{Ph}]^{\mathrm{tbe}} = -0.98$, $[\mathrm{S}]^{\mathrm{tbe}} = -0.6$, $[\mathrm{N}]^{\mathrm{tba}} = -0.035$, $[\mathrm{Cl}]^{\mathrm{tba}} = [\mathrm{Br}]^{\mathrm{tba}} = 0.00$ by definition.[29,33-35] For the complexes $R_2Sn(SPy)_2$, we obtained $\Delta E_{\mathrm{calcd}}$ values of $|2.80|$ and $|2.48|$ mm s^{-1}, respectively, for R = Alk and R = Ph, while for the complexes $R_2SnX(SPy)$, $\Delta E_{\mathrm{calcd}}$ is $|2.94|$ mm s^{-1} when R = Alk and $|2.57|$ mm s^{-1} when R = Ph. The agreement between experimental and calculated ΔE values is very satisfactory and justifies the assignment of *trans*-octahedral and trigonal-bipyramidal structures to our complexes.

Compound **15** crystallizes in the monoclinic space group $P2_1/n$. The atomic parameters are given in Table 2 and bond lengths and angles in Table 3. The atoms bound to tin form a distorted trigonal bipyramid with sulfur and two C(phenyl) atoms occupying the equatorial positions, whereas Cl and N(pyridine) are in axial positions (Fig. 1). The polyhedron around tin is comparable with that found in $Me_2SnCl(S_2CNMe_2)$.[36] The Sn–Cl distance corresponds to values for covalent bonds.[36,37] The angles N(1)–Sn(1)–S(1) [64.8(1)°] and Cl(1)–Sn(1)–N(1) [156.1(1)°], involving atoms of the rigid chelate ring, deviate strongly from the ideal values; still more acute N–Sn–S angles exist in $Ph_2Sn(SPy)_2$ [60.88(8)° and 60.52(8)°].[31] The values of the other angles are near those expected for a trigonal bipyramid (see Table 3). The tin atom is 0.15 Å below the plane through the atoms Sn(1), C(11), C(21) and S(1). Figure 2 shows the unit cell. Intermolecular dis-

Table 6 ^{1}H NMR spectral data [δ (ppm)] for diorganotin(IV) derivatives of 2-mercaptopyridine $R_2Sn(SPy)_2$ and $R_2SnX(SPy)$ and of PySSPy (**16**)

		SPy				
Compound	R	H-3	H-4	H-5	H-6	Solvent
1[a]	1.02 s	7.29 d	7.44 t	6.93 t	8.08 d	$CDCl_3$
	0.98 s	7.29 d	7.52 t	6.99 t	8.12 d	$CDCl_3$/DMSO-d_6
2	1.39 d, 2.02 sep[b]	7.32 d	7.45 t	6.94 t	8.21 d	$CDCl_3$
3	0.78–1.66 m	7.31 d	7.45 t	6.93 t	8.10 d	$CDCl_3$
	0.78–1.61 m	7.29 d	7.53 t	7.01 t	8.15 d	$CDCl_3$/DMSO-d_6
4	1.99 d, 1.66 d, 2.01 sep	7.32 d	7.44 t	6.93 t	8.10 d	$CDCl_3$
5	1.36 s	7.31 d	7.42 t	6.91 t	8.16 d	$CDCl_3$
6	1.09–2.14 m	7.29 d	7.43 t	6.94 t	8.19 d	$CDCl_3$
	1.08–2.15 m	7.30 d	7.59 t	7.08 t	8.30 d	$CDCl_3$/DMSO-d_6
7	7.20–7.97 m	—[c]	—[c]	6.79 t	8.09 d	$CDCl_3$
	7.31–7.28 m, 7.72–7.69 m	7.39 d	7.54 t	6.93 t	8.09 d	$CDCl_3$/DMSO-d_6
8[a]	1.09 s	7.33 d	7.62 t	7.07 t	7.93 d	$CDCl_3$
	1.02 s	7.38 d	7.69 t	7.15 t	8.24 d	$CDCl_3$/DMSO-d_6
9	1.43–d, 2.17 sep	7.32 d	7.59 t	7.05 t	8.01 d	$CDCl_3$
10	0.87–1.99 m	7.31 d	7.61 t	7.06 t	7.94 d	$CDCl_3$
11	1.10–1.02 m, 1.71 d, 2.18 sep	7.31 d	7.60 t	7.05 t	7.95 d	$CDCl_3$
12	1.43 s	7.32 d	7.59 t	7.05 t	8.09 d	$CDCl_3$
	1.36 s	7.46 d	7.82 t	7.27 t	8.34 d	$CDCl_3$/DMSO-d_6
13	1.33–2.39 m	7.30 d	7.59 t	7.05 t	8.04 d	$CDCl_3$
14	1.32–2.29 m	7.30 d	7.59 t	7.05 t	8.03 d	$CDCl_3$
15	7.36–7.45 m, 7.65–7.97 m	—[c]	7.63 t	7.10 t	8.08 d	$CDCl_3$
	7.24–8.15 m	—[c]	—[c]	7.00 t	8.45 d	DMSO-d_6
16	—	7.64–7.54 m		7.11 t	8.45 d	$CDCl_3$
	—	7.64 d	7.81 t	7.29 t	8.51 d	DMSO-d_6

[a] Coupling constants $^2J(^{119}Sn-^1H)$ in $CDCl_3$/DMSO-d_6: **1**, 77.8/78.8; **8**, 73.8/92.0. [b] Abbreviation: sep, septet, [c] Overlap.

tances smaller than the van der Waals radii do not exist.

The structural proposals derived from the infrared spectra are consistent with the results of the X-ray structure determinations and they correspond with the conclusions from the Mössbauer measurements that the structures of all compounds of each series are in principle the same. The A, G and H bands of the compounds $R_2Sn(SPy)_2$ (Table 5) are shifted by up to 13 cm^{-1} to higher wavenumbers in comparison with those of PySSPy (**16**).[21] This can be correlated with the formation of N→Sn coordination. A similar shift was observed in $MesSb(SPy)_2$ (Mes = mesityl), in which the existence of N→Sb coordination was confirmed by X-ray diffraction structure determination.[38, 39] Only one type of ligand band was observed, indicating that both SPy ligands are bound in the same way to tin. In the infrared spectra of the compounds $R_2SnCl(SPy)$ the A-, G- and H-type bands are shifted to slightly higher wavenumbers, and a significant shift of the C- and D-type bands to higher wavenumbers is also observed. This more pronounced shifting should indicate a stronger N→Sn coordination effected by the chloro ligands at tin. Similar differences have been observed between $Me_2Sn(Ox)_2$ and $Me_2SnCl(Ox)$ (HOx = 8-hydroxyquinoline);[40] in this context it is noteworthy that the Sn–N distance in compound **15** is about 0.2 Å shorter than the Sn–N distances in $Ph_2Sn(SPy)_2$.[31]

Structure in solution

The IR spectra of solutions of compounds **1–15** in $CDCl_3$ showed no significant differences of the A- to D-type bands compared with those in the solid state, and therefore the data were not included in Table 5. (Other bands overlap with solvent bands or are structurally irrelevant.) From the similarity it is inferred that the intramolecular N→Sn coordination established for the solid state is retained in solution; this applies to both series, $R_2Sn(SPy)_2$ and $R_2SnCl(SPy)$.

Table 7 ^{13}C NMR spectral data for diorganotin(IV) derivatives of 2-mercaptopyridine $R_2Sn(SPy)$ and $R_2SnX(SPy)$ and of PySSPy (**16**)

	δ (ppm)										
	R				SPy						
Compound	C-1	C-2	C-3	C-4	C-2	C-3	C-4	C-5	C-6	Solvent	$^1J(^{119}Sn-^{13}C)$ (Hz)
1	7.1				163.2	124.5	136.8	117.9	146.3	$CHCl_3$	598
	5.9				161.1	122.7	135.8	116.8	145.1	$CDCl_3$/DMSO-d_6	608
2	33.4	21.1			164.5	124.9	136.8	117.8	146.8	$CDCl_3$	572
3	28.3	26.6	26.4	13.7	163.9	124.7	136.7	117.8	146.5	$CDCl_3$	559
	24.5	26.1	24.2	11.8	161.2	122.4	135.4	116.4	144.9	$CDCl_3$/DMSO-d_6	n.o.[a]
4	37.9	26.7	26.2		163.8	124.6	136.7	117.8	146.6	$CDCl_3$	n.o.
5	43.5	31.0			164.0	124.7	136.5	118.1	147.1	$CDCl_3$	n.o.
6	44.7	31.0	29.0	26.8	164.5	124.8	136.7	117.8	146.7	$CDCl_3$	549
7	148.3.	134.3	128.3	128.6	164.6	124.1	137.9	117.9	144.3	$CDCl_3$	768
	146.4	132.7	126.9	127.3	162.2	122.4	136.9	116.9	143.1	$CDCl_3$/DMSO-d_6	n.o.
8	6.3				164.2	123.8	138.9	119.0	145.2	$CDCl_3$	558
	8.5b				162.2	123.9	138.4 b	118.6	146.4	DMSO-d_6	n.o.
9	30.5	20.7/20.5			165.3	124.0	138.7	118.7	146.0	$CDCl_3$	509
10	27.6	26.2	25.9	13.5	164.8	123.9	138.8	118.8	145.5	$CDCl_3$	516
11	38.1	26.2	26.0		164.9	124.0	138.7	118.8	145.5	$CDCl_3$	509
12	42.4	30.2			165.9	124.0	138.6	118.5	146.7	$CDCl_3$	456
	41.2	29.8			163.2	123.4	139.8	119.5	147.7	DMSO-d_6	n.o.
13	42.9	30.8	28.6	26.5	165.6	123.8	138.7	118.7	146.0	$CDCl_3$	468
14	42.5	30.5	28.6	26.4	165.6	124.0	138.6	118.6	146.3	$CDCl_3$	473
15[b]	141.0	135.2	129.0	130.3	164.2	123.7	139.4	119.5	146.2	$CDCl_3$	n.o.
	147.1	139.8	129.1	130.2	162.7	123.9	140.7	120.3	142.6	DMSO-d_6	n.o.
	147.5	134.0	128.2	127.4	162.6	123.7	139.0	119.0	145.1	DMSO-d_6	n.o.
16					158.5	120.9	137.2	119.3	149.3	$CDCl_3$	
					157.3	121.6	137.9	119.4	149.6	DMSO-d_6	

[a] Abbreviation: n.o., not observed. [b] Two sets of signals were observed in DMSO-d_6 solution; see text.

These findings are supported by the NMR spectra. The ^1H NMR signals of the SPy ligands, which were assigned according to the assignments in MeSPy,[41,42] appeared in ranges typical for the thiol form of the ligand (Table 6), and the number of signals as well as the intensity ratios correspond with those expected for monomeric species in solution. In comparison with compound **16**, the $\delta(^1H)$ values of the ligand protons H-4, H-5, and H-6 in $R_2Sn(SPy)_2$ (Table 6) are shifted to high field; the appreciable shift of H-6, which is located next to N, can be attributed to the formation of the $N \rightarrow Sn$ bond, and consequently indicates the existence of a chelate ring in the monomeric compounds. Similar shifting occurs in the ^1H NMR spectra of organotin oxinates and was also correlated with the formation of $N \rightarrow Sn$ coordination and chelation.[23,43–45] In $R_2SnX(SPy)$ an upfield shift of $\delta(^1H)$ of H-6 with relation to $R_2Sn(SPy)_2$ and compound **16** is observed. This presumably is effected by the electronegative ligand X and the increased Lewis acidity of tin. The H-3, H-4 and H-5 signals show nearly no change in relation to compound **16**.

The ^{13}C NMR signals (Table 7) of the SPy ligands which were assigned according to Refs 26, 42, 46 and 47 corroborate the results obtained from the ^1H NMR spectra. Compared with the $\delta(^{13}C)$ values of compound **16**, the ligands are bonded in the thiol form. The C-6 atoms in both series of compounds $R_2Sn(SPy)_2$ and $R_2SnX(SPy)$ in $CHCl_3$ solution show, in relation to compound **16**, an upfield shift of 2.2–5.0 ppm which indicates $N \rightarrow Sn$ coordination. The C-2 and C-3 atoms show a downfield shift of 2.7–6.4 ppm and this can also be correlated with the existence of $N \rightarrow Sn$ coordination, but in addition is caused partly by the decrease of electron density by the S–Sn bond. Similar shift effects were observed in the ^{13}C NMR spectrum of protonated pyridine (upfield shift of C-6 signal, downfield shift of C-3 and C-4),[48] as well as in the spectra of RHgSPy[49]

Table 8 ^{119}Sn NMR spectra of diorganotin(IV) derivatives of 2-mercaptopyridine (HSPy)

Compound	Solvent	δ (ppm)
1	$CDCl_3$	−124[a]
	$CDCl_3$/DMSO-d_6	−134
2	$CDCl_3$	−123
	$CDCl_3$/DMSO-d_6	−132
3	$CDCl_3$	−125
4	$CDCl_3$	−137
5	$CDCl_3$	−83
	$CDCl_3$/DMSO-d_6	−94
6	$CDCl_3$	−163
7	$CDCl_3$	−300
	$CDCl_3$/DMSO-d_6	−300
7	$CDCl_3$	−300[a]
	$CDCl_3$/DMSO-d_6	−300
8	$CDCl_3$	−61
	DMSO-d_6	−108/−148
9	$CDCl_3$	−67
10	$CDCl_3$	−77
11	$CDCl_3$	−75
12	$CDCl_3$	−90
	DMSO-d_6	−96
13	$CDCl_3$	−102
14	$CDCl_3$	−101
15	$CDCl_3$	−201
	DMSO-d_6	−241/−300

[a] Ref. 24.

and R_2SbSPy.[38] Measurements in deuterated dimethyl sulfoxide (DMSO-d_6) and in DMSO-d_6-$CDCl_3$ mixtures showed analogous upfield and downfield shifts, indicating that the N→Sn coordination is retained in the presence of the donor solvent molecules. The similarity of the $\delta(^{13}C)$ values of C-3, C-4 and C-5, and mainly the analogous upfield and downfield shifting of C-6 and C-2, respectively, indicate that the SPy ligands are bonded in all the compounds **1**–**15** in solution in the same manner, i.e. they form a four-membered chelate ring.

In the ^{13}C NMR spectrum of compound **15** in DMSO-d_6 solution two sets of $\delta(^{13}C)$ signals (Table 7) and in the ^{119}Sn NMR spectrum two $\delta(^{119}Sn)$ signals (Table 8) are observed. Considering the monomeric character of compound **15** and the $\delta(^{119}Sn)$ values being about 40 and 100 ppm, respectively, at high field in comparison with $\delta = -201$ ppm in $CDCl_3$, we assume that an equilibrium exists between 1:1 and 1:2 complexes of compound **15** and DMSO molecules. In this respect it is interesting to note that compound **15** can be recovered undecomposed from the solution in DMSO-d_6. Broad $\delta(^{13}C)$ signals for C-4 and CH_3 and two $\delta(^{119}Sn)$ signals (Table 8) in the appropriate NMR spectra of compound **8** in DMSO-d_6 solution indicate the existence of an analogous equilibrium.

^{119}Sn NMR signals of $R_2Sn(SPy)_2$ were observed in $CDCl_3$ solution between −123 and −137 ppm (R = alkyl, except t-butyl). The signals of the appropriate $R_2SnX(SPy)$ compounds appear to shift about 60 ppm towards higher field (Table 6), what would be consistent with a lower coordination number of tin in the latter compounds. The measured $\delta(^{119}Sn)$ values do not fit clearly into the reported ranges of $\delta(^{119}Sn)$ values of six-coordinated (−125[50] or −210[51] to −400 ppm) and five-coordinated organotin compounds (about −90 to −200 ppm).[50,51] Considering the usual differences between alkyltin and aryltin compounds (about 120–150 ppm[50,52]), the measured values are generally low in the appropriate range, or are even below the assumed lower limit. However, it appears questionable whether it is justified to try to fit the $\delta(^{119}Sn)$ values of the diorganotin thiolato complexes into the given shift ranges, since they were derived from organotin compounds with O-bonded and also halide ligands. Bond polarities of Sn–S bonds are lower than those of Sn–O bonds and the strong +*M* effect of O is missing. Therefore the central tin atom is less shielded than in comparable compounds with O-bonded ligands and $\delta(^{119}Sn)$ values are expected at lower field. We found similar tendencies of shifting in other organotin thiolato complexes (results will be published separately); it appears that specific range of δ values of organotin thiolato complexes should be established. Thus the $\delta(^{119}Sn)$ values of $R_2Sn(SPy)_2$ and of $R_2SnX(SPy)$ complexes in $CHCl_3$ seem to show good consistency with the presence of six- and five-coordinated tin in these compounds. The $\delta(^{119}Sn)$ values of $R_2Sn(SPy)_2$ complexes in DMSO are only a little shifted to low field as compared with shifts in $CHCl_3$, indicating that no appreciable increase of the coordination number had occurred.

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